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“पुराने को छोड़ नये के तरफ”

Jawaharlal Nehru

“Step Out From the Old to the New”

IS 504-13 to 16 (2003): Chemical Analysis of Aluminium and its Alloys, Part 13: To 16 [MTD 28: Methods of Chemical Analysis of Non-Ferrous Metals]



“ज्ञान से एक नये भारत का निर्माण”

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“ज्ञान एक ऐसा खजाना है जो कभी चुराया नहीं जा सकता है”

Bhartrhari—Nitiśatakam

“Knowledge is such a treasure which cannot be stolen”

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भारतीय मानक
एल्युमिनियम और उसके मिश्रधातुओं का
रासायनिक विश्लेषण

भाग 13 से 16
(दूसरा पुनरीक्षण)

Indian Standard
CHEMICAL ANALYSIS OF
ALUMINIUM AND ITS ALLOYS

PARTS 13 TO 16
(*Second Revision*)

ICS 71.040.50 : 77.120.10

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BUREAU OF INDIAN STANDARDS
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NEW DELHI 110002

FOREWORD

This Indian Standard (Parts 13 to 16) (Second Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Methods of Chemical/Instrumental Analysis of Non-ferrous Metals Sectional Committee had been approved by the Metallurgical Engineering Division Council.

This standard was first published in 1954 and subsequently revised in 1963. This revision of the standard covers following parts:

- | | |
|---------|--|
| Part 13 | Determination of sodium by atomic absorption and flame emission spectrophotometric methods |
| Part 14 | Determination of beryllium by AAS and spectrophotometric methods |
| Part 15 | Determination of zirconium by gravimetric and spectrophotometric methods |
| Part 16 | Determination of lithium by atomic absorption and flame emission spectrometric methods |

In view of the increasing use of aluminium alloys for various industrial applications, the need for standardized test methods for aluminium alloy to determine sodium, beryllium, zirconium and lithium were found necessary.

The standard although revised in parts is being printed in as a single publication for the convenience of users.

The composition of the Committee responsible for formulation of this standard is given in Annex. A.

For the purpose of deciding whether a particular requirement of this standard is complied with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

Indian Standard

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

PART 13 DETERMINATION OF SODIUM BY ATOMIC ABSORPTION AND FLAME EMISSION SPECTROPHOTOMETRIC METHODS

(*Second Revision*)

1 SCOPE

This standard (Part 13) determination of sodium in pure aluminium and aluminium 13.5 percent silicon alloys in the concentration level of 0.02 percent by atomic absorption and flame absorption spectrophotometric methods.

2 REFERENCES

The standard listed below contain provisions which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreement based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards:

<i>IS No.</i>	<i>Title</i>
264 : 1976	Nitric acid (<i>second revision</i>)
1070 : 1992	Reagent grade water (<i>third revision</i>)
1817 : 1961	Methods of sampling non-ferrous metals for chemical analysis
10332 : 1982	Hydrofluoric acid, aqueous

3 SAMPLING

The samples shall be drawn and prepared in accordance with IS 1817.

4 QUALITY OF REAGENTS

Unless specified otherwise, analytical grade reagents and double distilled or double deionized water shall be employed for the test.

5 PROCEDURE

5.1 Outline of the Method

The method is applicable for aluminium metals or aluminium-silicon alloys for concentrations of 0.02 percent sodium or less. After dissolution of the sample, the solution is aspirated into an air-acetylene flame. The measurements are then made by atomic absorption or flame emission methods.

5.2 Reagents

5.2.1 Double Distilled or Double Deionized Water (see IS 1070)

NOTE — The water used for the test must be deionized and kept in a plastic bottle. All the apparatus used (platinum, plastic, quartz and glassware) must be washed in hydrochloric acid ($rd = 1.18$) and then in distilled and deionized water. The use of double deionized water is preferable to avoid sodium contamination, use the same grades of reagents and double, deionized water. Avoid using mouth pipettes since sodium occurs in nature saliva. Use of automatic pipette is suggested.

5.2.2 Concentrated Nitric Acid ($rd = 1.33$) (see IS 264)

5.2.2.1 Dilute nitric acid — Dilute concentrated nitric acid with an equal volume of double deionized water.

5.2.3 Hydrofluoric Acid ($rd = 1.1$) (see IS 10332)

NOTE — Hydrofluoric acid is extremely irritating and corrosive to skin and mucous membrane and produces severe skin burns which are slow to heal. In case of contact with skin, wash well with water and seek medical help immediately.

5.2.4 Sodium, Standard Solution (1 000 mg), weigh 0.254 g of sodium chloride previously heated for half an hour at 400°C and cooled. Dissolve in double deionized water and make upto 100 ml in a volumetric flask. Transfer and store in a polyethylene container.

5.2.5 Sodium, Standard Solution (10 mg) — Prepare a dilute solution of 100 mg/l sodium by diluting 10 ml of sodium (1 000 mg) (see 5.2.4) to 100 ml with double deionized water. Dilute 10 ml of this solution to 100 ml using double deionized water to obtain sodium, standard solution of 10 mg. Store in a polythene container.

NOTE — The dilute solutions should be prepared fresh and should not be stored for more than one week. Use the same set of reagents for the preparation of standards and sample solutions.

5.3 Procedure

5.3.1 Preparation of Calibration Curve

Place in each of seven platinum crucibles samples of pure aluminium metal of 0.435 g (for the analysis of aluminium 13 percent silicon) or 0.500 g (for other aluminium samples). Attack cold with 10 ml of nitric

acid rd = 1.33, diluted to half (*see* 5.2.2.1); then with care add 2.5 ml of hydrofluoric acid (rd=1.1) (*see* 5.2.3). Cover the crucibles with platinum or plastic lids. When the effervescence ceases, heat moderately on a hot plate until the dissolution is complete without allowing it to concentrate. Allow to cool and using plastic funnels transfer each of the samples to a series of 50 ml plastic volumetric flasks numbered 1 to 7. In each of this add respectively 0, 1, 3, 5, 6, 8 and 10 ml of standard solution of sodium (10 mg) (*see* 5.2.5) corresponding to 0, 0.002, 0.006, 0.010, 0.012 0, 0.016 0 and 0.020 percent sodium with respect to alloy. Make upto mark with distilled or double deionized water and shake. Determine the sodium content by atomic absorption or flame emission spectrophotometry.

5.3.2 Atomic Absorption Spectrophotometry

Use atomic absorption spectrophotometer as per the manufacturer's instructions. Allow the sodium hollow cathode lamp to stabilize for 10 min or longer as needed. Use air acetylene flame and adjust the instrument parameters like wavelengths. Flow rate of air and fuel (acetylene), burner height and monochromator slit width as per the recommended procedure. The measurements are to be made at 589.0 nm.

5.3.3 Flame Emission Spectrophotometry

Measure the emission of sodium at 589 nm using an air-acetylene flame using an atomic absorption spectrophotometer equipped with emission accessory. Measure the emission signal and use burner rotation if necessary to reduce the path length. In this case, the calibration must be carried out with the same setting of the instrument. Set the zero reading while aspirating distilled (or deionized) water or blank. Aspirate each standard and the unknown and record their emission intensity. With some instruments, the 100 percent reading is set with the most concentrated solution. If

the calibration curve is not linear and shows a curvature, suitably dilute both the test solutions and the standards. Follow the manufacturer's instructions regarding the operation of the instrument and selection of operating conditions.

NOTE — In the case of internal standard instruments, add a known excess amount of lithium (1 000 mg) to both the samples and standards and dilute to volume with double deionized water. Use of lithium at a concentration of 10 times the maximum expected concentration of sodium may be satisfactory. The lithium emission is measured at 670.8 nm. Prepare the calibration curve as for the direct reading instrument but record the ratio of Na/Li emission intensities.

5.4 Dissolution of the Sample

Attack 0.5 g of the alloy weighed accurately to the nearest 0.001 g in a platinum crucible in the same manner as described in the case of standards.

Transfer the resulting solution to a 50 ml plastic volumetric flask. Make upto mark with double deionized water. Determine sodium by AAS or flame emission spectrometry as described in 5.3.2 and 5.3.3.

NOTE — The above procedure makes use of hydrofluoric acid containing solutions. The atomic absorption and flame emission instrument should be equipped with sample introduction system resistant to hydrofluoric acid solutions.

To prevent fouling of the burners due to high salt content aspirate between each analysis 1:1 hydrochloric acid solution followed by deionized water and then double deionized water.

EXPLANATORY NOTE

It is also possible to dissolve the samples using hydrochloric acid. However, this may render the graphite carbon insoluble and lead to the precipitation of silica. The analysis of sodium after silica removal is reported to give lower results. For samples not containing silica, a direct dissolution and estimation from hydrochloric acid medium may be satisfactory.

Indian Standard

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

PART 14 DETERMINATION OF BERYLLIUM BY AAS AND SPECTROPHOTOMETRIC METHODS

(Second Revision)

1 SCOPE

This standard (Part 14) covers the determination of beryllium in aluminium alloys in the range of 0.01 to 5.0 percent by atomic absorption and derivative spectrophotometric method.

2 REFERENCES

The standards listed below contain provisions which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision and parties to agreement based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards:

<i>IS No.</i>	<i>Title</i>
265 : 1993	Hydrochloric acid
1070 : 1992	Reagent grade water (<i>third revision</i>)
1817 : 1961	Methods of sampling non-ferrous metals for chemical analysis

3 SAMPLING

Samples shall be drawn and prepared in accordance with IS 1817.

4 QUALITY OF REAGENTS

Unless otherwise specified, analytical grade reagents and distilled water (*see* IS 1070) shall be employed for the test.

5 DETERMINATION OF BERYLLIUM BY AAS METHOD

5.1 Outline of the Method

After dissolution of the sample in hydrochloric acid, beryllium is estimated by AAS using nitrous oxide/acetylene flame in presence of lanthanum oxide as ionization suppresser.

5.2 Reagents

5.2.1 Hydrochloric Acid (rd = 1.18) (*see* IS 265)

5.2.2 Hydrogen Peroxide (30 volume percent)

5.2.3 Standard Beryllium Solution (200 mg/l) —

Prepare a stock solution of beryllium by dissolving beryllium sulphate (2.33 g) in 1 l using 10 ml of concentrated sulphuric acid (rd = 1.84).

5.2.4 Beryllium, Standard Solution (20 mg) — Dilute 10 ml of beryllium standard solution (200 mg/l) (*see* 5.2.3) into 100 ml using distilled water in a one-mark volumetric flask and mix well. Prepare solution fresh for every day.

NOTE — Beryllium and its salts are highly toxic. Avoid mouth pipetting of the beryllium containing solutions. Store the solutions containing beryllium in a separate container and dispose off the solution according to local regulations.

5.2.5 Aluminium, Standard Solution (50 g/l) — Dissolve 5 g of metal in 100 ml of hydrochloric acid (rd = 1.18) (*see* 5.2.1). Add 6 drops of hydrogen peroxide (*see* 5.2.2). After dissolution, reduce volume to about 75 ml. Allow to cool. Filter through a 7 cm medium fast filter paper (Whatman No. 540 or equivalent). Make upto 100 ml in a one mark 100 ml volumetric flask with water.

5.2.6 Lanthanum Oxide Solution (100 g/l) — Dissolve 100 g of lanthanum oxide in 200 ml of hydrochloric acid (*see* 5.2.1) and dilute to 1 l with distilled water.

5.3 Procedure

5.3.1 Preparation of Calibration Curve

Into a series of 100 ml volumetric flasks, place 10 ml of aluminium solution (50 g/l) and 0, 5, 10, 20, 40 ml of standard beryllium solution (20 µg/ml).

The above corresponds to 0, 0.1, 0.2, 0.4, 0.8 mg of beryllium corresponding to 0, 0.02, 0.04, 0.08, 0.16 percent of beryllium in the initial sample. Add 10 ml of lanthanum oxide solution (100 g/l). Dilute exactly to 100 ml and mix well. Aspirate into atomic absorption unit and measure the absorbance.

NOTE — Use burette and exercise due care since beryllium solutions are highly toxic.

5.3.2 AAS Measurements

The determination of beryllium must be made on a nitrous oxide-acetylene flame with lanthanum oxide as ionization suppresser. This also reduces the depressive effect of aluminium.

The special and operating conditions must be selected according to the manufacturer's instructions. Measurements are made at 234.9 nm using nitrous oxide/acetylene flame. The safety precautions on the use of nitrous oxide/acetylene flame must be observed.

5.4 Procedure for Test Sample

Dissolve 5 g of metal in 100 ml of hydrochloric acid ($rd = 1.18$). Add 6 drops of hydrogen peroxide (30 volume percent) (see 5.2.2). After dissolution, reduce the volume to about 75 ml. Allow to cool. Filter, if necessary and make upto 100 ml with distilled water.

Place 10 ml of this solution in a 100 ml graduated volumetric flask and add 10 ml of 100 g/l lanthanum solution (see 5.2.6). Make upto mark with distilled water.

Determine beryllium by AAS as described under preparation of calibration curve (see 5.3.1).

5.5 Calculations

Calculate the concentration of berillium using the relation

$$\text{Beryllium, ppm} = \frac{A}{B} \times 10^3$$

where

A = concentration of beryllium in $\mu\text{g/ml}$ of the measured solution, and

B = weight of the sample taken in g.

NOTE — Beryllium and its compounds are highly toxic. Carry out the work in well ventilated fume hood. The atomic absorption unit must be provided with good exhaust in order to avoid any danger due to toxic beryllium fumes. For higher concentrations of beryllium, the spectrophotometric method can be employed.

6 DETERMINATION OF BERYLLIUM BY DERIVATIVE SPECTROPHOTOMETRIC METHOD

6.1 Outline of the Method

This method involves the determination of beryllium using thorin as the chromophoric reagent using a derivative spectrophotometric procedure.

6.2 Reagents

6.2.1 Beryllium Standard Solution (200 mg/l) — Prepare by dissolving 2.33 g of beryllium sulphate in 1 l using 10 ml of concentrated sulphuric acid ($rd = 1.84$).

6.2.2 Beryllium Standard Solution (20 mg/l) — Dilute 10 ml of beryllium standard solution (see 6.2.1) in 100 ml of volumetric flask using distilled water. Prepare solution fresh.

NOTE — Beryllium solutions are highly toxic. See note under 5.3.1.

6.2.3 Sulphuric Acid (3 Percent) — Dilute 30 ml of concentrated sulphuric acid ($rd = 1.84$) in 1 l of distilled water.

6.2.4 EDTA, Disodium Salt (5 Percent) — Dissolve 5 g of disodium salt of ethylene diamine tetraacetic and (EDTA) in distilled or deionized water and make upto 100 ml in a volumetric flask. Transfer to a polyethylene bottle.

6.2.5 Ammonium Chloride, 50 Percent (m/v) — Dissolve 50 g of ammonium chloride in 60 ml of water. Warm to room temperature and dilute to 100 ml in a volumetric flask.

6.2.6 Sodium Hydroxide (20 Percent) — Dissolve 20 g of sodium hydroxide in 80 ml of distilled water and make upto mark with distilled water after cooling the solution to the room temperature. Transfer to a polyethylene bottle and store.

6.2.7 Thorin (0.01 Percent) — Dissolve 100 mg of thorin (2 hydroxy 3.6 disulfo-1 naphthylazo benzene arsonic acid) in 100 ml of distilled water.

6.3 Procedure

6.3.1 Preparation of Calibration Graph

Into a set of five 50 ml volumetric flask add 10 ml of aluminium (50 g/l) and then add 0, 2.5, 5.0, 7.5, 10 ml of beryllium (200 $\mu\text{g/ml}$) (see 6.2.1), add 3 ml of 50 percent ammonium citrate, 10 ml of 5 percent EDTA solution and 4 ml of 0.1 percent thorin solution to each of the beakers. Adjust the pH of these solution to 10 ± 0.1 (use pH meter) with 20 percent sodium hydroxide. Make upto 50 ml. After half an hour, Scan the first derivative spectrum between 520 nm and 450 nm with $A = 10$ nm. Read out the A/d values for the solution at 493.8 nm.

Plot the calibration curve of A/d versus concentration.

6.4 Test Solutions

Dissolve 5 g of aluminium alloy in 100 ml of hydrochloric acid ($rd = 1.18$). Add 6 drops of hydrogen peroxide. After dissolution, reduce the volume to about 75 ml. Allow to cool. Filter, if necessary and make upto 100 ml with distilled water.

Place 10 ml of this solution in a calibrated flask and proceed as described in the preparation of calibration curve. Record the first derivative data at 439.8 unit and calculate the concentration of beryllium.

6.5 Calculation

Calculate the concentration of beryllium in ppm as given below:

$$\text{Beryllium, ppm} = \frac{A}{B} \times 500$$

where

A = concentration of beryllium, in $\mu\text{g/ml}$, of the measured solution, and

B = amount of the alloy, in g.

This is suitable for determination of beryllium in the range of 0.1 percent to 0.4 percent. For other concentrations, make a suitable dilution of sample and reduce the amount of aluminium in the standards.

7 DETERMINATION USING BERYLLON II (METHOD II)

Beryllium in aluminium alloys can be determined by spectrophotometric method using beryllon.

7.1 Procedure

One gram of an aluminium alloy sample is dissolved without heating in 50 ml of 20 percent sodium hydroxide. If the sample dissolution is slow, it may be speeded up by warming the solution towards the end of dissolution. The alkaline solution along with the precipitate is transferred to 250 ml flask and make upto the mark. The solution is allowed stand for a few hours and filtered. A suitable aliquot is placed in a 100 ml volumetric flask. The solutions are diluted to about

30 to 40 ml with distilled water, neutralized with 1, 1 hydrochloric acid till the appearance of turbidity. They can be clarified by the addition of 5 percent sodium hydroxide (NaOH).

To the resulting weakly alkaline solution are added 20 ml of 0.05 percent sodium hydroxide and 10 ml of 0.02 percent aqueous solutions of beryllon II. The solution is made upto mark with water and mixed well. After 10 min, the absorbance is measured at 620 nm. the concentration is calculated from a calibration curve prepared from pure aluminium.

7.2 Calculation

The beryllium concentration can be calculated using:

$$\text{Beryllium, ppm} = \frac{A}{B} \times \frac{100}{v} \times 250$$

where

A = concentration of Be, in $\mu\text{g/ml}$, of measured solution,

B = weight of alloy, in g,

250 = volume of solution containing the alloy, and

v = volume of the aliquot used for the measurement.

Indian Standard

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

PART 15 DETERMINATION OF ZIRCONIUM BY GRAVIMETRIC AND SPECTROPHOTOMETRIC METHODS

(Second Revision)

1 SCOPE

This standard (Part 15) covers the determination of zirconium in aluminium alloys by gravimetric and spectrophotometric methods, depending on their concentration levels.

2 REFERENCES

The standards listed below contain provisions which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreement based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards:

<i>IS No.</i>	<i>Title</i>
264 : 1976	Nitric acid (<i>second revision</i>)
265 : 1993	Hydrochloric acid
1070 : 1992	Reagent grade water (<i>third revision</i>)
1817 : 1961	Methods of sampling non-ferrous metals for chemical analysis
10332 : 1982	Hydrofluoric acid, aqueous

3 SAMPLING

The samples shall be drawn and prepared in accordance with IS 1817.

4 QUALITY OF REAGENTS

Unless specified otherwise, analytical grade reagents and distilled water (*see* IS 1070) shall be employed for the test.

5 DETERMINATION OF ZIRCONIUM (AND HAFNIUM) BY GRAVIMETRIC METHOD

5.1 Outline of the Method

This procedure is applicable for alloys containing at least 5 to 30 mg of zirconium (0.2 percent and above). For lower concentrations, the spectrophotometric method may be adopted.

NOTE — Zirconium is not sensitive by AAS but can be determined using plasma emission methods like Inductively Coupled Plasma Atomic Emission Spectrometric method (ICPAES method) or Directly Coupled Plasma Atomic Emission Spectrometric method (DCPAES method).

5.2 Reagents

5.2.1 Concentrated Hydrochloric Acid (rd = 1.18) (*see* IS 265)

5.2.2 Mandelic Acid (150 g/l) — Dissolve 15 g of mandelic acid in 40 ml of water in a 100 ml beaker. Filter through a 7 cm medium fast filter paper (Whatman No. 540 or equivalent) into a 100 ml one-mark volumetric flask. Make upto the mark with distilled water.

5.2.3 Mandelic Acid, Wash Solution — Dissolve 2 g of mandelic acid in 100 ml of (1 : 10) hydrochloric acid.

5.2.4 Absolute Alcohol (95 Percent Ethanol)

5.2.5 Diethylether

5.3 Procedure

Take 1 g of the alloy in a 150 ml beaker, add 10 ml of concentrated hydrochloric acid (rd = 1.18) diluted 1 : 1. Warm, if necessary, to assist the dissolution of the sample. Transfer to a 100 ml volumetric flask and wash the beaker with 10 ml of concentrated hydrochloric acid (rd = 1.18) added in portions and make upto the mark using distilled water. Transfer 50 ml of the solution to a 250 ml beaker. Add 25 ml of mandelic acid (*see* 5.2.2) dropwise, slowly and with constant stirring. Digest the precipitate for at least 30 min at 80-90°C on a hot plate or water bath and let stand at room temperature for 1 h. If the sample aliquot contains 10 mg or less zirconium or in presence of sulphate, the digestion should be carried out for 1 to 2 h, and the solution allowed to stand for 4 to 5 h. or preferably overnight before filtration. Filter through a 7 cm low ash filter paper (Whatman No. 542 or equivalent). Wash with 50 to 100 ml of wash water containing 2 g of mandelic acid in (1 : 10) HCl (*see* 5.2.3). Transfer the precipitate to a weighed platinum crucible. Heat on a low flame to dry and char the filter paper and then strongly at 800 to 1 000°C weigh as ZrO_2 .

NOTE — When the concentration of zirconium is low, it is possible to estimate zirconium as zirconium tetramandellate. For this, precipitate zirconium as tetramandellate as described in 5.3. Filter the precipitate through a weighed sintered glass crucible. Wash the precipitate with a solution of (1 : 10) hydrochloric acid saturated with zirconium tetramandellate and then with three 10 ml portions of 95 percent ethanol and finally with two 10 ml portions of diethylether. Dry approximately at 110°C, cool and weigh the precipitate as zirconium tetramandellate (mass in mg of tetramandellate precipitate $\times 0.1771$ = mass of ZrO_2).

5.4 Calculation

Calculate the percentage of zirconium using:

$$\text{Zirconium, percent (m/m)} = \frac{A}{B} \times 100 \times X$$

where

A = weight of ZrO_2 precipitate, in g,

B = weight of alloy in g represented by the aliquot, and

X = gravimetric factor for $\text{ZrO}_2 = \text{Zr/ZrO}_2$.

6 DETERMINATION OF ZIRCONIUM (AND HAFNIUM) BY A SPECTROPHOTOMETRIC METHOD

6.1 Outline of the Method

Zirconium is separated from the other constituents of the aluminum alloy by extraction of the sample aliquot by TOPO (see 6.2.6) in cyclohexane from nitric acid medium. The colour is developed in Tri-*n*-octyl Phosphine Oxide (TOPO) solution by the addition of pyrocatechol violet and measured spectrophotometrically at 655 nm.

6.2 Reagent

6.2.1 Zirconium, Standard Solution (1 000 mg/l) — Transfer 0.100 g of zirconium of minimum 99.9 percent (*m/m*), weighed to the nearest 0.001 g to a small platinum dish. Add about 5 ml of double distilled water and then 40 percent hydrofluoric acid (*rd* = 1.13) dropwise until the metal has dissolved. Add a few drops of nitric acid (*rd* = 1.42) heat it gently to expel the oxides of nitrogen and then cool. Add 10 ml of concentrated sulphuric acid (*rd* = 1.84). Evaporate the solution to the fumes of sulphuric acid and then continue to heat the solution for 10 min more and cool. Add about 20 ml of water and transfer the solution to a 100 ml one-mark standard mark. Add 20 ml of concentrated sulphuric acid (*rd* = 1.84). Cool the solution to room temperature. Dilute to the mark and mix well. Store in a polyethylene bottle.

6.2.2 Zirconium, Standard Solution B (10 mg/l) — Dilute 5 ml of zirconium standard solution *A* (see 6.2.1) to 500 ml with distilled water. Make up to mark and mix well. Prepare fresh.

6.2.3 Concentrated Sulphuric Acid (*rd* = 1.84)

6.2.4 Hydrofluoric Acid (*rd* = 1.13) (see IS 10332)

NOTE — Hydrofluoric acid is extremely irritating and corrosive to skin and mucous membranes and produces severe skin burns which are slow to heal. In case of contact with skin, wash well with water and seek medical advice.

6.2.5 Concentrated Nitric Acid (*rd* = 1.42) (see IS 264)

6.2.6 Tri-*n*-octyl Phosphine Oxide (TOPO) (0.1M) —

Dissolve 1.93 g of TOPO in 50 ml of cyclohexane. This is sufficient for ten determinations. The solution must be freshly prepared.

NOTE — Collect the organic solutions containing (TOPO) in a separate container. Dispose them off safely according to local regulations. It is possible to strip zirconium using sulphuric acid (dilute) and reuse TOPO for further experiments after distilling off cyclohexane.

6.2.7 Nitric Acid (7N) — Dilute 44 ml of concentrated nitric acid (*rd* = 1.42) (see IS 264) to 100 ml in a volumetric flask.

6.2.8 Pyridine

6.2.9 Pyrocatechol Violet (0.2 Percent)

6.2.10 Hydrochloric Acid, Dilute — Dilute 50 ml of hydrochloric acid (*rd* = 1.18) to 100 ml with distilled water (see IS 1070).

6.3 Procedure

6.3.1 Preparation of Calibration Graph

Add separately 0, 2, 4, 6, 8, 10 ml of standard zirconium solution (10 µg/ml) (see 6.2.2) to each of six 100 ml conical flasks fitted with B 17 or B 24 glass sockets and stopper.

Add 11 ml of concentrated nitric acid (*rd* = 1.42) to each flask and dilute to 25 ml with calculated quantity of distilled water. Add 5 ml of TOPO (0.1M in cyclohexane) (see 6.2.6), stopper the flask and shake for 15 min in a mechanical shakers. After equilibration, transfer the contents of the flask to a graduated measuring cylinder or to a separating funnel. Zirconium will be found in the top organic layer. Transfer 1 ml of the organic phase to a dry 25 ml calibrated flask. Add 10 ml of absolute alcohol (95 percent), 1.5 ml of pyrocatechol violet solution (0.2 percent) and add 5 ml of pyridine. Dilute the solution to mark with absolute ethanol, wait for 5 min for the colour to develop and determine the optical density at 655 nm with a 1 cm cell.

NOTE — If a rotary shaker is not available, the test can be carried out using six good quality separating funnels. After equilibration for 15 min, drain off the lower aqueous phase and use the remaining organic phase for spectrophotometric measurements as described in 6.3.1.

6.3.2 Preparation of Test Solutions — Take 1 g of the sample weighed to the nearest 0.001 g in a 150 ml beaker. Add 10 ml of dilute hydrochloric acid (1 : 1), warm the mixture gently to assist dissolution. When the sample has dissolved add 5 ml of diluted sulphuric acid (1 : 4), evaporate the solution to the fumes of sulphuric acid. Cool and add 11 ml of concentrated nitric acid (*rd* = 1.42) and add 14 ml of water. Heat the mixture to boiling to dissolve the residue and cool the solution. Make up to 25 ml.

Take a suitable aliquot of the sample depending on the concentration of zirconium. For lower concentrations of zirconium, take the entire sample and for higher concentrations, take a suitable aliquot. Add sufficient amount of nitric acid (7N) (*see* 6.2.7) to make the total volume to 25 ml. Add 5 ml of TOPO (0.1 M) (*see* 6.2.6). Shake well in a mechanical shaker as described in 6.3.1. Allow the layers to separate. Transfer 1 ml of the organic phase (top layer) to a dry 25 ml calibrated flask and continue as described above under the preparation of calibration curves (*see* 6.3.1).

Run a blank experiments with pure aluminium side by side and deduct the blank value from the measured value. Calculate the zirconium content from the calibration graph.

NOTE — For lower concentrations of zirconium, take 2 ml of organic phase for the development of colour.

6.4 Calculation

Calculate the concentration of zirconium in the sample using the relation:

$$\text{Zirconium, ppm} = \frac{A}{B}$$

where

- A = concentration of zirconium, in $\mu\text{g/ml}$, and
- B = weight, in g, of the alloy in the aliquot taken.

NOTE — The result obtained represents the total of zirconium plus hydrofluoric acid. If individual concentration of hydrofluoric acid is needed, other techniques like ICPAES or neutron activation analysis may be employed.

Indian Standard

CHEMICAL ANALYSIS OF ALUMINIUM AND ITS ALLOYS

PART 16 DETERMINATION OF LITHIUM BY ATOMIC ABSORPTION AND FLAME EMISSION SPECTROMETRIC METHODS

(*Second Revision*)

1 SCOPE

This standard (Part 16) covers the determination of lithium in aluminium alloys in the concentration range between 0.1 and 5 percent.

2 REFERENCES

The standards listed below contain provisions which through reference in this text, constitute provisions of this standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreement based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards:

<i>IS No.</i>	<i>Title</i>
265 : 1993	Hydrochloric acid
266 : 1993	Sulphuric acid (<i>third revision</i>)
1070 : 1992	Reagent grade water (<i>third revision</i>)
1817 : 1961	Methods of sampling non-ferrous metals for chemical analysis

3 SAMPLING

The samples shall be drawn and prepared in accordance with IS 1817.

4 QUALITY OF REAGENTS

Unless otherwise specified, analytical grade reagents and distilled water (*see* IS 1070) shall be employed for the test.

5 DETERMINATION OF LITHIUM BY ATOMIC ABSORPTION AND FLAME EMISSION METHODS

5.1 Outline of the Method

The aluminium lithium alloy is dissolved in hydrochloric acid and lithium is determined by aspiration of the solution into air-acetylene flame using atomic absorption or flame emission method.

5.2 Reagents

5.2.1 High Purity Concentrated, Hydrochloric Acid (rd = 1.18) (*see* IS 265).

5.2.1.1 Dilute hydrochloric acid, prepare by dilution

of concentrated acid with an equal volume of double distilled water (*see* IS 1070).

5.2.2 Double Distilled Water (*see* IS 1070)

5.2.3 Aluminium Standard Solution (1 000 mg/l) — Weigh 1.000 g to the nearest 0.001 g of aluminium metal of 99.9 percent (*m/m*) minimum purity and transfer to a 400 ml beaker. Add 30 ml of hydrochloric acid (rd = 1.18) diluted to 1 : 1 and heat to complete dissolution. In the case of very pure aluminium, a small drop of mercury can be added before the addition of hydrochloric acid to hasten the dissolution. Filter the solution through a 7 cm rapid filter paper (Whatman No. 541 or equivalent) into a 400 ml beaker. Wash the filter with 100 ml of warm water. Add 85 ml of concentrated hydrochloric acid (rd = 1.18) to the filtrate, cool and transfer to a 1 000 ml one mark volumetric flask. Make up to the mark with double distilled or deionized water and store in a polyethylene bottle.

NOTES

1 Mercury is highly poisonous and has appreciable vapour pressure. It must be stored in strong, tightly closed containers. Liquid mercury, if used, must be transferred in such a manner that a spill can be contained and thoroughly cleaned up at once.

2 Discard mercury in accordance with local regulation. It may be stored under water in a tightly closed container, pending disposal. It is possible to purify mercury by treatment with 5 percent nitric acid in presence of oxygen and subsequent washing with water to remove the excess of acid followed by distillation under vacuum.

5.2.4 Aluminium Standard Solution (100 mg/l) — Pipette 100 ml of the aluminium standard reference solution (*see* 5.2.3) into a 1 000 ml one-mark volumetric flask and add 90 ml of hydrochloric acid (rd = 1.18). Dilute to approximately 800 ml with double distilled or deionized water, cool, make up to the mark, mix and store in a polyethylene bottle.

NOTE — The diluted solution should not be stored for more than one month.

5.2.5 Lithium, Standard Solution (1 000 mg/l) — Dissolve 5.324 g of Li_2CO_3 previously dried at 105°C in a minimum amount of hydrochloric acid and transfer into a 1 000 ml one-mark volumetric flask and add 40 ml of hydrochloric acid (rd = 1.18). Dilute to

approximately 800 ml with double distilled or deionized water, cool, make up to the mark mix well and store in a polyethylene bottle.

5.2.6 Lithium, Standard Solution (100 mg/l) — Pipette 100 ml of lithium standard (see 5.2.5) into a 1 000 ml one mark volumetric flask and add 40 ml of hydrochloric acid ($rd = 1.19$). Dilute to approximately 800 ml with double distilled or deionized water, cool, make up to the mark, mix well and store in a polyethylene bottle.

5.2.7 Lithium, Standard Solution (10 mg/l) — Pipette 100 ml of lithium standard solution (100 mg/l) (see 5.2.6) into a 1 000 ml one-mark standard flask and dilute with double or deionized water to the mark, mix and store in a polyethylene bottle.

5.2.8 Lithium, Standard Solution (1 mg/l) — Pipette 100 ml of lithium standard solution (10 mg/l) (see 5.2.7) into a 1 000 ml one-mark volumetric flask and dilute with distilled or deionized water to the mark, mix well and store in a polyethylene bottle.

NOTE — The diluted solution 5.2.7 and 5.2.8 should not be kept for longer than one week.

5.2.9 Sodium Standard Solution (1 000 mg/l) — Dissolve 0.254 g of NaCl previously heated to 400°C and cooled in distilled water and dilute to 100 ml.

5.3 Procedure for Atomic Absorption Measurements

5.3.1 Preparation of the Range of Standard

Place 10 ml of the standard solution of aluminium (1 000 mg/l) (see 5.2.3) in five 100 ml flasks and mark this as 1, 2, 3, 4 and 5. Place in each of them respectively 0, 10, 20 ml of the solution of lithium (1 mg/l) and 5, 10, 20 of lithium (10 mg/l) and make up to 100 ml with double distilled or deionized water. This produces a range of standards containing 100 µg/ml of aluminium and respectively 0, 0.1, 0.2, 0.5, 1.0, 2.0 µg/ml of lithium. Measure the absorbance of the solution using an atomic absorption spectrophotometer at 670.8 nm using lithium hollow cathode lamp as the radiation source and air acetylene flame for atomization. The optimization of the working conditions should be made as per the manufacturer's instructions.

NOTE — Proceed for atomic absorption measurements as per the instruction manual of the instrument. Allow the lithium hollow cathode lamp to stabilize for 10 min or longer as needed. Use air-acetylene flame and adjust the instrument parameters like wavelength, flow rate of air and fuel (acetylene), burner height and monochromator slit width as per the recommended procedure. Use burner rotation, if needed in order to reduce the path length in the case of higher concentrations. In such cases, the calibration curves must be obtained under the same conditions.

5.3.2 Measurement of Test Solution

Proceed as given in 7 and 7.1.

6 DETERMINATION OF LITHIUM BY FLAME EMISSION SPECTROMETRY

6.1 Preparation of the Range of Standards

Place 10 ml of the standard aluminium solution (1 000 mg/l) (see 5.2.3) in six 100 ml flasks marked 0, 1, 2, 3, 4 and 5. Place in each of them respectively. 0, 10, 20 ml of lithium standard solution (1 mg/l) (see 5.2.8) and 5-10-20 ml of the solution of lithium standard (10 mg/l) (see 5.2.9). Make up to 100 ml with distilled water. Measure the emission of lithium at 670.8 nm, using an air-acetylene flame of an atomic absorption unit equipped with flame emission measurements. Use burner rotation, if necessary in order to reduce the path length. Measure the emission signal. Set the zero reading while aspirating distilled water or blank. Aspirate each standard and the unknown recording their emission intensity. With some instruments, the 100 percent reading is set with the most concentrated solution. If the calibration curve is not linear and shows a curvature, suitably dilute the test solutions and standards. Follow the manufacturer's instructions regarding the operation of the instrument and the selection of operating conditions.

NOTE — In the case of internal standard instrument, add a known excess amount of sodium (1 000 mg/l) to both the samples and standards and dilute to volume with double distilled water. Use of sodium at a concentration of 10 µg/ml will be sufficient. The sodium emission is measured at 590 nm. Prepare the calibration curve as for the direct reading instrument but record the ratio of Li/Na emission intensities.

6.2 Measurement of Test Solution

7 PREPARATION OF TEST SOLUTION (FOR BOTH ABSORPTION AND EMISSION MEASUREMENTS)

Take 2.5 g of alloy. Pour gradually on to the sample which has been previously covered with water. Forty ml of hydrochloric acid ($rd = 1.18$). Warm, if necessary, to assist the dissolution. When the dissolution is complete, make up to 500 ml with double distilled or deionized water. Take 10 ml of the solution and make up to 100 ml with distilled water and 10 ml of concentrated hydrochloric acid. Take 10 ml of the preceding solution and make up to 50 ml with 5 ml of concentrated hydrochloric acid ($rd = 1.18$) and double distilled water. One ml of the solution contains 100 µg of the alloy. The solution also contains 1 µg/ml of lithium for a lithium content of 1 percent and will be suitable for analysis in the range of 0 to 2 percent. For higher concentrations, suitable burner rotation may be

made or the solutions or both the samples and standards suitably diluted in order that the aluminium content in them is the same.

Aspirate the solution into the flame under the conditions described for the calibration of the standard. Measure the absorbance (or the emission intensities) and calculate the concentrations.

7.1 Calculation

Calculate the percentage of lithium as follows:

$$\text{Lithium, percent by mass} = \frac{A}{B \times 104}$$

where

A = concentration, in $\mu\text{g/ml}$, of lithium in the final measured solution, and

B = concentration, in g/ml , of the alloy in the final measured solution.

NOTE — In the case of instruments using internal standard, add a constant amount of sodium at a final concentration of $10 \mu\text{g/ml}$ in both the samples and standards.

ANNEX A

(Foreword)

COMMITTEE COMPOSITION

Methods of Chemical/Instrumental Analysis of Non-ferrous Metals Sectional Committee, MTD 28

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Central Electrochemical Research Institute, Karaikudi, Tamil Nadu
Controllerate of Metals, Ichapur, West Bengal

Defence Mettrallurgical Research Laboratory, Hyderabad

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Indian Aluminium Co Ltd, Kolkata
Indian Copper Development Center, Kolkata
India Government Mint, Ministry of Finance, Mumbai
Indian Lead Zinc Development Center, New Delhi
Indian Metals and Ferro Alloys Ltd, Therubeli

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National Aluminium Co Ltd, Angul, Bhubaneshwar
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This Indian Standard has been developed from Doc : No. MTD 28 (4297-4300).

Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

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